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Mesochem: Chemical Dynamics on a Mesoscopic Scale

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Most chemically stable organic materials age through changes on the mesoscopic scale (from 10 nm to 10 mm). Examples include the slow crystallization of polymers, changes in particle size distributions with age, and the swelling of pressed powders. We began the Mesochem project to develop a new mesoscopic modeling capability for organic materials, including polymers, molecular crystals, and filled polymer composites. Our goal was to develop and validate novel mesoscopic modeling techniques that are well suited for materials of interest to LLNL's nation security mission, such as high explosives, binding agents, and foams.

Although LLNL has a world-class ability to model material properties on the atomic and macroscopic scales, the structures characteristic of soft matter occur at the mesoscopic scale, between these two limiting regimes. Our current ability to model the aging and dynamical properties of mesoscopic systems is quite limited. In this project, we developed flexible models of organic matter on the mesoscopic scale. This has helped LLNL to better achieve a wide range of programmatic goals, while generating a scientifically unique model of mesoscale matter.

The complex structure characteristic of soft matter leads to material behavior on a variety of timescales that are much longer than the 10-ns practical timescale limit of molecular dynamics. In order to address this problem, we used dissipative particle dynamics (DPD), an intermediate-length-scale approach to dynamics. .

We developed methods to determine an accurate mesoscopic representation of a system based on underlying microscale calculations by combining electronic structure and molecular dynamics simulations to derive effective DPD interactions. These activities are described in publication 1, 2, and 5 below. In these papers we conducted a series of advanced electronic structure calculations on the TATB molecule, for use in dissipative particle dynamics calculations.

We then undertook a DPD simulation of the anisotropic thermal expansion of the TATB molecule. This is described in publication 4 below. We were able to shed insight into the anisotropic thermal expansion of TATB using a first principles approach to dissipative particle dynamics.

Other work in the project centered on the development of mesoscopic models of polymer crystallization. Having conducted extensive ordinary molecular dynamics studies of crystallization in vinylidene fluoride, we discovered that vinylidene fluoride forms ordered crystals within 10 to 20 ns when cooled extremely rapidly from the melt. This is the first time that bulk, three-dimensional polymer crystallization has been calculated through molecular dynamics. This work is described in publication 3 below.

In summary, the mesochem project led to successful mesoscopic models of the thermal expansion of TATB crystals. This project is of programmatic interest, and further work is being carried out in the stockpile stewardship program. The project also led to the discovery of ultrafast polymer crystallization. We are continuing to study this new

phenomenon through large-scale molecular dynamics simulations on our largest computers.

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Publications

1. "Ab Initio Based Force Field and Molecular Dynamics Simulations for Crystalline TATB", Richard H. Gee, Szczepan Roszak, Laurence E. Fried, and Krishnan Balasubramanian, *Journal of Chemical Physics,* (accepted 2004), **UCRL-JC-152577.**

2. "Molecular Interactions of TATB Clusters", Szczepan Roszak, Richard H. Gee, Krishnan Balasubramanian, and Laurence E. Fried, *Chemical Physics Letters,* 374, 286-296(2003), **UCRL-JC-152312.**

3. Richard H. Gee and Laurence E. Fried, "Ultrafast crystallization of polar polymer melts", J. Chem. Phys. 118 (8): 3827-3834 (2003), **UCRL-JC-146807.**

4. "Gee, R. H., S. Roszak, and L. E. Fried, "Theoretical Studies of Interactions Between TATB Molecules and the Origins of Anisotropic Thermal Expansion and Growth", 33rd International Annual Conference of ICT, Page 30, 2002,**UCRL-JC-146807.**

5. "Internal rotation of amino and nitro groups in TATB", M. R. Manaa , R. H. Gee, and L. E. Fried, J. Phys. Chem. A106 (37): 8806-8810(2002), **UCRL-JC-146895.**